

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08L 27/12, 81/06, 79/08	A1	(11) International Publication Number: WO 95/21216 (43) International Publication Date: 10 August 1995 (10.08.95)
(21) International Application Number: PCT/US94/00940 (22) International Filing Date: 4 February 1994 (04.02.94) (71) Applicant: E.I. DU PONT DE NEMOURS & COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: HAGIWARA, Minori; 1904-60-201, Shimosakunobe, Takatsu-ku, Kawasaki, Kanagawa 213 (JP). KIWA, Kenji; 631-1-205, Kanamori, Machida, Tokyo 194 (JP). OGITA, Tatsuya; 2-2-10-503, Nijigaoka, Asou-ku, Kawasaki, Kanagawa 215 (JP). D'HAENENS, Luc, Germain, Pierre, Joseph; Twaalfkameren 68, B-9000 Gent (BE). (74) Agents: BURGESS, Richard, H. et al.; E.I. du Pont de Nemours & Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CN, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PRIMER COMPOSITION AND USE OF THE SAME COMPOSITION FOR COATING METAL SURFACES WITH A FLUORORESIN (57) Abstract A primer for a fluororesin coating composition comprising fluororesin, aluminum flake and more polyether sulfone than polyamideimides.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE

PRIMER COMPOSITION AND USE OF THE SAME COMPOSITION FOR COATING METAL SURFACES WITH A FLUORORESIN

BACKGROUND OF THE INVENTION

5 The present invention relates to a primer composition for adhering a fluororesin coating onto a metal surface, and a method for coating a metal surface with a fluororesin, using the primer composition.

 Because of its excellent properties in chemical resistance, heat resistance, non-stickiness, and the like, fluororesins are used as preferred coating materials
10 for metal surfaces, for example, in applications which include linings for chemical units, which are required to be corrosion resistant: linings for rice cookers, and cooking utensils that are required to be corrosion resistant and non-sticky. However, the excellent non-stickiness results in insufficient adhesion to the metal surface, and a variety of methods have been used up to
15 now for improving the adhesion to metal surfaces.

 When coating a metal surface with a fluororesin, powder coating is normally carried out for coating the fluororesin, in that a thicker application can be made compared to that of a fluororesin coating made by spray coating, so as to give good corrosion resistance and excellent non-stickiness to the coated
20 surface, as well as providing resistance to the formation of pinholes reaching as deep as the substrate. however, this approach still does not solve the problem of resistance to sticking to the substrate due to the non-stickiness which characterizes the fluororesin, so that powder coating of the metal surface with a fluororesin calls for using, in addition to the above inorganic acid primer, a
25 primer for the fluororesin powder coating containing Organic adhesives, such as polyamideimides, polyimides, polyether sulfones, epoxy resins, and the like, followed by powder coating a fluororesin. However, none of these processes provides optimum adhesion and corrosion resistance when used for a primer for a fluororesin powder coating. That is, a thick powder coating application results
30 in a coated film with a large internal stress resulting in the deficiencies of cohesive failure of the primer and a layer-layer delamination between the primer and top coat (powder coating), problems which remain unsolved.

 Thermoplastic fluororesins which are film-forming fluororesins, such as tetrafluoroethylene/perfluoroalkyl vinyl ether copolymers (PFA),
35 tetrafluoroethylene/hexafluoropropylene copolymers (FEP), and the like, are

capable of exhibiting fluidity at or above their melting points and of adhering to metals with an adhesion strength too weak to be of any practical use. Thus, the conventional approach has been to chemically or physically roughen the metal surface, followed by a thermal fusion or adhering with the intermediary of an adhesive or primer between the fluororesin film and the metal. These procedures, while exhibiting satisfactory initial adhesion strength, have had low heat resistance making it difficult to maintain adhesion strength in service above 200°C, due to the thermal degradation and thermal decomposition of the adhesive itself or decay of the anchoring effect. Thus, it has been difficult to adhere a fluororesin film to metal, and if any adhesion was provided at all, it was of a weak adhesion strength or had undesirable heat resistance.

Primers used as such adhesives have contained such materials as polyamideimides (PAI), polyimides (PI), polyphenylene sulfones (PPS), polyether sulfones (PES), and mica, such as in EP 343051 - Sumitomo Electric, and Japanese Kokai 58(83)-19702. However, none of the prior art seems to have found the best proportions of the right ingredients for optimum primers to be used with PFA powder coats or film laminating.

The coating of a metal surface, especially for cookware, with a fluororesin by powder coating the metal surface with a fluororesin or adhering a fluororesin film to the metal surface requires assuring secure adhered surfaces without treating the metal surface with an chromic acid or similar inorganic acids that raise toxicity questions. Also needed is improved adhesion between the metal surface and the fluororesin, good heat resistance, corrosion resistance, and durability.

SUMMARY OF THE INVENTION

The present invention provides a primer composition for a fluororesin coating comprising a solution or a dispersion in an organic solvent, of a polyether sulfone, a polyamideimide, and/or a polyimide, a fluororesin, and a metal powder, in which the proportion of the polyether sulfone: polyamideimide and/or polyimide is from 55:45 to 95:5 and the ratio of the total polyether sulfones and polyamideimides and/or polyimides to the fluororesin is 20:80 to 70:30 by weight, and in which the metal powder is in the form of flake and is present in an amount of 1-15% based on the solids of the composition by weight.

DETAILED DESCRIPTION

Extensive studies by the present inventors in order to solve the above problems have led to the finding that adhesion to a metal surface can be considerably improved, and a fluoro-resin coating having excellent heat resistance and durability can be provided as well. by the generation of a primer-applied layer on the metal surface using for a primer composition a fluoro-resin coating comprising a solution or a dispersion in organic solvent of a polyether sulfone, polyamideimide and/or polyimide; a fluoro-resin, and a metal powder, followed by powder coating a fluoro-resin, or else sintering the primer and hot-melting a thermoplastic fluoro-resin film. This finding has led to the completion of this invention.

That is, the present invention relates to a primer composition for a fluoro-resin coating comprising a dispersion in organic solvent of a polyether sulfone, polyamideimide and/or polyimide, a fluoro-resin, and a metal powder.

The present invention also relates to a process for coating a metal surface with a fluoro-resin comprising applying to said metal surface a primer composition for the fluoro-resin coating obtained by dissolving or dispersing in an organic solvent a polyether sulfone, a polyamideimide and/or a polyimide, a fluoro-resin, and a metal powder and applying the fluoro-resin to the resultant primed layer.

The present invention also relates to a process for adhering a thermoplastic film to a metal surface comprising applying to the metal surface a primer composition for a fluoro-resin coating, obtained by dispersing in an organic solvent a polyether sulfone, polyamideimide and/or a polyimide, a fluoro-resin, and a metal powder, sintering the primer on the resultant primer layer, and hot melting a thermoplastic fluoro-resin film.

The present invention provides a most optimum coating composition, as a primer for a rice cooker or chemical lining application. which requires extensive corrosion resistance; and, as a primer to provide excellent corrosion resistance and adhesion for carrying out a powder coating of a fluoro-resin, for example, FEP and PFA.

As described above, the present invention uses a coating comprising the two binder components of a polyether sulfone and polyamideimide and/or a polyimide, plus FEP or PFA and a metal powder, thereby solving problems which have been of concern heretofore, such as food hygiene problems,

problems of adhesion to the base surface, layer-to-layer adhesion, and corrosion resistance.

The primer composition for a fluororesin coating of this invention comprises a fluororesin as a component, preferably a perfluororesin of an readily-fusible, PFA, FEP, or a blend of these two. The use of these resins provides preferred results in terms of adhesion to the base metal material and interlayer adhesion to a top coat, either a fluororesin powder coated film or a laminated thermoplastic fluororesin film. Heating PFA and FEP beyond their melting point resists pinhole formation because of their lower melt viscosity as compare to polytetrafluoroethylene (PTFE) and also facilitates flow into narrow sections when they are applied to a base material roughened by blasting, or the like, so as to facilitate adhesion, which is responsible for their use being preferred.

Effective binders for adhesion to metals are known to be polyamideimides, polyimides, polyether sulfones, polyphenyl sulfides, and the like. Frequently used base materials such as aluminum, steel, stainless steel, aluminum and stainless steel plated materials, and the like, in particular, steel and stainless steel, and the like, are more difficult to surface roughen compared to aluminum, therefore, they are more difficult to adhere. Among these binders, one which provides the most optimum adhesion to steel-type base materials is polyether sulfone. However, the use of a fluororesin primer with a polyether sulfone binder cannot be said to provide good interlayer adhesion, as discussed above.

The present inventors discovered that blending two binder types, a polyamideimide and/or a polyimide and a polyether sulfone provides increased coating strength, thereby generating a coated film which resists a cohesive failure.

The primer composition of this invention is designed to let the polyether sulfone migrate during sintering towards the base metal material side and to let the fluororesin migrate towards the top of the coated film, thereby performing its function as the coated film. If this separation progresses excessively, there is a danger of generating internal stresses in the coated film; if the film is subjected to conditions under which there is an external force, the possibility of crack formation between the polyether sulfone and the fluororesin arises; and these conditions could result in the delamination of the coated film. However, the

primer composition of this invention further comprises a metal powder which hinders the separation of the polyether sulfone from the fluororesin so as to maintain the condition of mixing of the two, thereby making it difficult to allow separation: moreover, the metal powder itself relaxes internal stresses preventing any adhesive failure from occurring.

In addition, the primer composition of this invention further comprises a polyamideimide and/or a polyimide, and conceivably the polyamideimide, which is a curing resin, securely solidifies while the above ideal conditions are maintained. Therefore, the composition resists softening even at high temperatures, so as to provide good corrosion resistance at high temperatures. This results in the provision of a coated film which can satisfactorily withstand stress due to temperature changes, and the like.

The polyether sulfone: polyamideimide and/or polyimide ratio, when a good coated film in the composition of this invention is generated, is within the range of 95:5 to 55:45 by weight. (Parts, proportions and percentages herein are by weight except where indicated otherwise.) Having an excessive amount of polyether sulfone tends to accelerate cohesive failure of the primer, thereby decreasing interlayer adhesion with the top coat. An excessive amount of polyamideimide will provide poor resistance to corrosion, so that even if the top coat itself is corrosion-resistant, exposure to severe corrosive conditions or damage to the coated film will result unfavorably in the coated film's delamination from the base substrate due to the penetration of water vapor or a solution, or the like, into the primer.

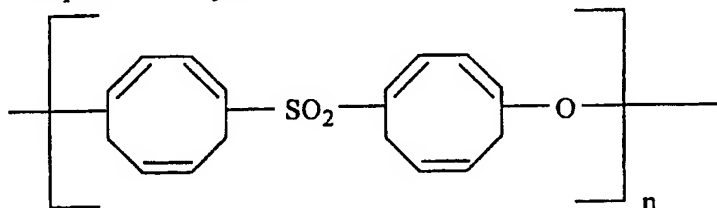
Particularly in the case of a steel-based substrate, Table 1 clearly shows that the adhesion of the polyamideimide is inferior to that of polyether sulfone, so that the use of a larger amount is not preferred.

The powder-coated FEP or PFA layer together with the primer coated layer is sintered at a temperature of at least 340°C, and the fact that the top coat is clear makes it undesirable to use a large amount of polyamideimide which is brown in color in applications requiring a good cosmetic appearance, such as in a rice cooker, or the like.

The ratio by weight of the total of the two binders, polyether sulfone and polyamideimide, in the composition of this invention to the fluororesin is 20:80 to 70:30. Excessive use of the fluororesin results in decreased adhesion to

the base substrate, while an insufficient amount of the fluororesin results in less fusion with the top coat, with a resultant decrease in interlayer adhesion.

The polyether sulfone which is component A for the composition of this invention comprises one represented by the following structural formula:



5

The polyamideimide and/or polyimide as components for the composition of this invention are specifically, for example those derived from trimellitic anhydride and methylene dianiline; trimellitic anhydride and oxydianiline; or trimellitic anhydride and metaphenylene diamine; aminobismaleimide, being used singly or in any mixture thereof. Particularly preferred components for the composition of this invention, from among these polyamideimides and/or polyimides, are those derived from trimellitic anhydride and methylene dianiline.

10

The metal powder, a component of the composition of this invention, is preferably of a flaky form. Any metal type can be used, but it is necessary to use a metal powder which is problem-free in terms of toxicity to humans for use in fabricating articles which come in contact with food, such as a rice cooker and cooking utensils, preferably, for example: aluminum, steel, tin, zinc, copper and the like; and alloys. For example, aluminum alloys, stainless steel, and the like.

15

The addition of this type of metal powder can be expected to improve thermal conductivity; in addition to the thermal conductivity aspect, it is necessary to be concerned with a type of metal which resists corrosion by way of an electro-corrosion reaction if the base material is, for example, steel: i.e., using an aluminum powder can prevent such corrosion. That is, it is well known that corrosion takes place by transferring electrical charges when a base substrate is corroded, so that adding a metal to the primer which is electrically less noble (a higher ionization tendency than Fe) can prevent the steel base material from corroding, which particularly favors the use of such a metal. The proportion of aluminum which best generates such a favorable primer coating is 2-10% by weight.

20

25

30

From the standpoint of the cosmetics of the surface coating, the type of metal powder and its shape should be selected accordingly. The metal powder is used based on the weight of the solids of the composition- in the range of 1-15%, preferably 2-10%.

5 The composition of this invention is optionally mixed with additives such as a viscosity regulator, a stabilizer, a colorant, and a dispersant.

The organic solvents which can be used include N-methyl pyrrolidone by itself: preferably mixed systems of N-methyl pyrrolidone with diacetone alcohol or xylene, and the like.

10 The composition of this invention is prepared by mixing the above components at the desired ratios and dispersing in a dispersing medium. The compositional ratio is adjusted so that the weight ratio of the total of the polyether sulfone and polyamideimide and/or polyimide: the fluororesin is 20:80 to 70:30.

15 The primer composition for a fluororesin coating prepared in this manner is applied to a metal surface by any coating method. The coatings method includes a variety of types, such as spray coating, spin coating, brush-coating, and the like.

20 The primer coated film thickness is preferably 5-15 microns in terms of the thickness after sintering.

25 The primer-coated metal surface is then dried. The drying is normally carried out at temperatures from ambient temperature to about 200°C, thereby generating a primer-coated layer on the metal surface after removal of any of the dispersion medium or other volatile matter from the primer composition for use in fluororesin coating.

The resultant primer-coated layer is then treated with a fluororesin. The fluororesin may be FEP, PFA, or a blend of FEP and PFA. The fluororesin is then applied to the primer-coated layer by means of powder coating followed by sintering the primer coated layer and the fluororesin-coated layer.

30 Sintering is carried out by the usual devices and methods for 10-40 minutes at temperatures of 350-400°C.

35 The present invention can also be carried out by replacing the fluororesin coating on the above primer-coated layer with a hot melt adhered fluororesin film on the sintered primer-coated layer, thereby coating the metal with the fluororesin.

The fluororesin films used herein can be those prepared from FEP, PFA, or a blend of FEP and PFA.

Embodiments of the present invention using the fluororesin film comprise drying the primer layer applied to the metal surface, sintering beyond
5 the temperature of the primer's melting point, mounting on top of the primer-coated layer a fluororesin film, and hot melt adhering, thereby generating an extremely securely adhered fluororesin coated layer on the metal surface.

The present invention is now specifically described by the following examples.

10 EXAMPLES

Example 1. Polyether sulfone (PES), polyamideimide (PAI), tetrafluoroethylene/hexafluoropropylene copolymer (FEP), and an aluminum flake powder was added to a blended solvent of N-methyl pyrrolidone and diacetone alcohol (2:1) followed by preparing a fluororesin primer composition
15 having the composition shown in Table 1. The composition had a viscosity ranging from 200-400 cps as measured by a B-type viscometer.

The FEP used had a composition of 85:15 by weight of tetrafluoroethylene/hexafluoropropylene.

PES was a VICTREX manufactured by the ICI Company.

20 PAI was a RHODEFTAL manufactured by Rhone Poulenc or a polyamideimide made by Phelps Dodge.

The resultant composition was sprayed onto a surface-degreased aluminum sheet to reach a thickness after sintering of 7-15 microns. The coated film was then dried followed by applying by electrostatically coating a powder
25 of tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer (PFA). The coated film thickness was adjusted so as to reach 80 microns after sintering in terms of the total coated film thickness. The PFA-coated film was sintered 20 minutes at an aluminum substrate temperature of 380°C.

The PFA used in this operation was a copolymer of 97:3 by weight of
30 tetrafluoroethylene/perfluorovinyl ether.

The equivalent of the PAI, which can be used to provide the PAI itself, is polyamic acid which can be partially, completely or not yet converted to PAI in the coating composition. It converts to PAI on curing the coating.

In preparing the above coated film, part of the surface of the aluminum
35 sheet was masked to generate a PFA-only layer of the top coat with no primer,

so as to allow 1 cm wide cross cuts covering both that section and the primed sections.

The resultant material was tested by: (a) boiling 15 minutes followed by measuring the peel strength of the coated film so as to investigate where the peel occurred; (b) spraying 5% brine for 144 hours followed by measuring the peel strength of the coated film and investigating where the peel occurred; (c) boiling 8 hours in a solution obtained by dissolving in 1 L of water, 25 g of Oden no Moto Extract, a fish and vegetable gumbo-type sauce, followed by cooling for 16 hours. The process was repeated for four days, after which the peel strength of the coating was measured. The results are summarized in Table 1.

Example 2. An aluminum, alloy-plated steel sheet was surface-degreased with acetone and spray coated to cover the surface of the steel plate with a primer obtained by dispersing a composition comprising PES:PAI at a ratio of 4:1 and the ratio of PES+PAI:FEP of 1:2, with an aluminum platelet content of 4% in a dispersion medium comprising N-methyl pyrrolidone and diacetone alcohol and adding a pigment thereto. The coated thickness was adjusted so as to reach a post-dry thickness of about 8 microns. The sample was dried for 15 minutes at 150°C followed by sintering in a sintering oven securely for 15 minutes at 350°C.

The PES, PAI, and FEP used in this example were identical to those used in Example 1.

After sintering the primer, a 25 micron thick PFA film was mounted on the primer followed by hot melt adhesion of this film at 350°C under a pressure of 5 kg/cm. The PFA film was securely adhered to the primer and the primer to the metal surface. The PFA film used in this example was a film prepared from the same resin as that used in Example 1.

An evaluation of the adhesion strength of the adhered product with respect to temperature changes was taken. The sample was held at 100, 150, 200, and 250°C. respectively, for 25, 50, or 100 hours, followed by carrying out a cross Erichsen test with 5 mm wide cuts to evaluate the adhesion strength.

TABLE I

Sample No.	PES:PAE	PES+PAI: FEP	Aluminum Content (%)	15-min Boiling	Peel Strength		(Peeled)	"Oden Extract"
					(Peeled)	Brine Spray 144 Hours Test		
1	10:0	1:1	5	10-20	(Base Substrate)	-	-	-
1A	10:0	1:1	0	400-500	(Between Layers)	-	-	-
2	10:1	1:1	0	1500-1600	(Between Layers)	800	(Between Layers)	-
2A	10:1	1:1	5	1500-1600	(Between Layers)	1500-1600	(Between Layers)	-
3	10:3	1:1	0	1500-1600	(Between Layers)	1500-1600	(Between Layers)	750
3A-1	10:3	1:1	5	1600-1800	(Between Layers)	1700-1800	(Between Layers)	-
3A-2	10:3	3:1	5	400-700	(Base Substrate)	-	-	-
3A-3	10:3	1:2	5	1600-1800	(Between Layers)	1700-1800	(Between Layers)	1300
3A-4	10:3	1:9	5	200-300	(Base Substrate)	-	-	-
4	10:5	1:1	0	1500-1600	(Between Layers)	1500-1600	(Between Layers)	750
5	10:10	1:1	0	1500-1600	(Between Layers)	1500-1600	(Between Layers)	750
6	5:10	1:1	0	1500-1600	(Between Layers)	1500-1600	(Between Layers)	-
6A	5:10	1:1	5	1700-1800	(Between Layers)	1700-1800	(Between Layers)	-
7	0:5	1:1	0	200-300	(Base Substrate)	-	-	-

NOTE: "-" indicates no test.

Example 3. Example 2 was repeated except for using an aluminum sheet.

5 Example 4. Example 2 was repeated except for using a stainless steel sheet.

10 Control 1. Example 3 was repeated except for eliminating PAI from the fluororesin primer.

Control 2. Example 3 was repeated except for removing the PES from the fluororesin primer.

15 Control 3. Example 4 was repeated except for eliminating PAI from the fluororesin primer.

Control 4. Example 4 was repeated except for removing the PES from the fluororesin primer.

20 Control 5. An aluminum alloy-plated steel sheet was shot-blasted followed by adhering PFA film by the intermediary of a heat resistant silane coupling agent.

25 Control 6. An aluminum alloy-plated steel sheet was coated with a highly heat-resistant silicone adhesive followed by adhering the PFA film.

30 Control 7. An aluminum sheet was shot-blasted followed by hot melt adhering a PFA film. Coatings obtained from these Examples were subjected to an adhesion strength test with a change in temperature to provide the results given in Table 2.

TABLE 2

°C. (Hrs)	EXAMPLES										
	2	3	4	5	6	7	8	9	10	11	
100°C. 25	◆	◆	◆	◆	◆	◆	◆	◆	○	○	
100°C. 50	◆	◆	◆	◆	◆	◆	◆	◆	○	○	
100°C. 100	◆	◆	◆	◆	◆	◆	◆	◆	○	○	
150°C. 25	◆	◆	◆	◆	◆	◆	◆	◆	Δ	○	
150°C. 50	◆	◆	◆	◆	◆	◆	◆	◆	Δ	○	
150°C. 100	◆	◆	◆	◆	◆	◆	◆	◆	Δ	○	
200°C. 25	◆	◆	◆	◆	Δ	◆	Δ	○	χ	χ	
200°C. 50	◆	◆	◆	◆	Δ	◆	Δ	○	χ	χ	
200°C. 100	◆	◆	◆	○	χ	○	χ	Δ	χ	χ	
250°C. 25	◆	◆	◆	χ	χ	χ	χ	χ	χ	χ	
250°C. 50	◆	◆	◆	χ	χ	χ	χ	χ	χ	χ	
250°C. 100	◆	◆	◆	χ	χ	χ	χ	χ	χ	χ	

In the Table:

◆ : Excellent:

○ : Good:

Δ : Fair:

χ : Poor.

As described above, a blend of polyether sulfone with a polyamideimide gives a very strong interlayer adhesion and also provides excellent heat-resistant adhesion when, exposed to high temperatures. This effect cannot be obtained if either PES or PAI is missing. The present invention is expected to find a broad
5 range of applications for covering metal sheet with a fluororesin film.

WHAT IS CLAIMED IS:

1. A primer composition for a fluororesin coating comprising a solution or a dispersion in an organic solvent, of a polyether sulfone, a polyamideimide, and/or a polyimide, a fluororesin, and a metal powder, in which the proportion
5 of the polyether sulfone: polyamideimide and/or polyimide is from 55:45 to 95:5 and the ratio of the total polyether sulfones and polyamideimides and/or polyimides to the fluororesin is 20:80 to 70:30 by weight, and in which the metal powder is in the form of flake and is present in an amount of 1-15% based on the solids of the composition by weight.
- 10 2. The primer composition of Claim 1 in which the metal powder is aluminum flake or aluminum alloy flake in an amount of 2 to 10% based on the solids of the composition by weight.
3. The primer composition for a fluororesin coating in Claim 1 in which the fluororesin is tetrafluoroethylene/hexafluoropropylene copolymer,
15 tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer, or a blend of the two.
4. A process for coating a metal surface with a fluororesin comprising applying to said metal surface a primer composition of Claim 1 and applying the fluororesin to the resultant primed layer.
5. A process for coating a metal surface with a fluororesin as set forth in
20 Claim 4 in which the fluorinated resin used in the primer composition for the fluororesin coating is tetrafluoroethylene/hexafluoropropylene copolymer, tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer, or a blend of the two.
6. A process for adhering a thermoplastic fluororesin film to a metal surface comprising applying to the metal surface a primer composition of
25 Claim 1 and applying onto said layer a thermoplastic fluororesin film by hot melt adhesion.
7. A process of Claim 6 in which the fluororesin used in the primer composition for the fluororesin coating is tetrafluoroethylene/hexafluoropropylene copolymer, tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer,
30 or a blend of the two.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/00940

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L27/12 C08L81/06 C08L79/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 10309 (DU PONT) 25 June 1992 see page 11; claims 1-8	
A	--- EP,A,0 389 966 (SUMITOMO ELECTRIC INDUSTRIES) 3 October 1990 see page 13 - page 14; claims 1-8	
A	--- EP,A,0 343 015 (SUMITOMO ELECTRIC INDUSTRIES) 23 November 1989 see page 7; claims 1-11 --- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

18 October 1994

Date of mailing of the international search report

- 9. 11. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Stienon, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/00940

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO,A,91 02773 (DU PONT) 7 March 1991 see page 10 - page 11; claims 1-12 -----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/00940

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9210309	25-06-92	US-A- 5230961	27-07-93
		US-A- 5240775	31-08-93
		AU-B- 651420	21-07-94
		AU-A- 9141091	08-07-92
		CN-A- 1064292	09-09-92
		EP-A- 0561981	29-09-93
		JP-T- 5509036	16-12-93
		TR-A- 25556	01-05-93
EP-A-389966	03-10-90	JP-A- 2251440	09-10-90
		JP-B- 6009909	09-02-94
		JP-A- 3159623	09-07-91
		CN-A- 1046121	17-10-90
		DE-D- 69011369	15-09-94
		US-A- 5106682	21-04-92
EP-A-343015	23-11-89	JP-A- 2089633	29-03-90
		US-A- 5009959	23-04-91
WO-A-9102773	07-03-91	US-A- 5079073	07-01-92
		US-A- 5049437	17-09-91
		AU-A- 6155290	03-04-91
		DE-D- 69005828	17-02-94
		DE-T- 69005828	16-06-94
		EP-A- 0489036	10-06-92
		ES-T- 2049039	01-04-94
		JP-T- 4507369	24-12-92